

Preparation of Allylsucrose

EDWARD L. GRIFFIN, JR., MILES J. WILLARD, JR.,
H. I. SINNAMON¹, PAUL W. EDWARDS, AND C. S. REDFIELD

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

This work was carried out to study the preparation of allylsucrose monomer in equipment of the type that might be used for its commercial production and also to produce allylsucrose monomer for laboratory studies and industrial samples.

Process variables in the preparation of allylsucrose monomer were studied in a small pilot plant. Approximately 60 gallons of good allylsucrose were produced for samples. The process and equipment used are described in detail. Improvements in the process which could be made in a production plant are recommended. A system for recovery of the allyl by-products is suggested. A production cost estimate is included.

A suitable production method which consistently produces good allylsucrose monomer was developed.

ALLYLSUCROSE is a light-amber viscous liquid prepared by allylation of sucrose. It has potentialities as a coating material, adhesive, drying oil, upgrader, and copolymer.

The optimum molar proportions of the reactants and the basic data for the reaction have been determined by Zief and Yanovsky (5). Their method consisted in reacting sugar, allyl chloride, sodium hydroxide, and water in molar proportions of 1:12:12:13.3 in a 1-gallon stainless steel autoclave, removing most of the salts and unreacted caustic in a single water wash, steam distilling to remove volatile by-products, washing to remove residual caustic and salts, and extracting the product with toluene.

The work described in this paper is a continuation of this study in a small pilot plant. It was carried out at the Eastern Regional Research Laboratory in cooperation with the Sugar Research Foundation. Preparation and purification of allylsucrose were studied, and a suitable method for producing good allylsucrose monomer was developed. The principal innovations over the process of Zief and Yanovsky (5) were the neutralization of residual caustic with phosphoric acid, instead of washing it out, and the substitution of vacuum drying and filtration for the toluene extraction step.

EQUIPMENT

Figure 1 shows diagrammatically the equipment used in the pilot plant, except the filter. The reactor (Figure 2) consists of a one-third jacketed 30-gallon stainless steel pressure vessel with 0.25-inch walls, 19.5-inch inside diameter, and 31-inch inside height. It has a 42-r.p.m., 1.5-inch wide anchor-type agitator which clears the walls by about 0.75 inch. Steam or cold water may be used separately in the jacket, or they may be mixed to give hot water at any temperature up to about 205° F. The reactor is equipped with a pressure gage, a sight glass, a rupture disk connected to an outside vent, and a recording thermometer

located in the center of the agitator shaft. The anchor-type agitator is required to prevent caking of solids on the bottom or sides of the reactor, but its arrangement in this reactor with a single bearing at the top allowed it to rock slightly under load and wear the packing excessively. It was therefore difficult to keep the agitator gland tight. Admixture by this agitator of the two liquid layers in the reactor was not considered satisfactory.

There is a vapor connection from the top of the reactor to a 15-square foot shell-and-tube condenser and a 30-gallon receiver. A dial thermometer is located in the vapor line just before the condenser. The reaction and all subsequent purification steps except filtration can be carried out in this pressure vessel. In about one half the runs, however, a 10-gallon glass-lined kettle having better agitation was used for the neutralization operation. This kettle had an anchor-type agitator which could be run at relatively higher speeds. Neutralization in the kettles was controlled by pumping a sample of the mixture continuously through a closed glass chamber containing pH meter electrodes.

Filtration was accomplished in a stainless steel horizontal plate pressure filter having a total filtration area of 1.22 square feet, divided between three operating plates and one scavenger plate.

Stainless steel or glass-lined equipment was used throughout the process. Dilute hydrochloric acid vapors formed by hydrolysis of allyl chloride have not as yet caused any appreciable damage, but a commercial installation might require a more resistant alloy in the condenser and receiver.

PROCESS

The optimum proportions of reactants as recommended by Zief and Yanovsky (5) were used for most runs. Figure 3 is a flow sheet of the best process for production of allylsucrose as developed in the pilot plant. The charge required per 100 pounds of product and the average yields and compositions of the resulting by-product fractions are shown on this flow sheet.

The charge used in the pilot plant is limited by the capacity of the reactor, which must hold the reacted materials plus sufficient water to dissolve the sodium chloride and caustic present after the reaction. The maximum charge that can be used in the 30-gallon reactor is about 191 pounds, as shown in the average material balance (Table II).

The reactor is checked for leaks between each run. Since allyl chloride is toxic, gas masks are used whenever allyl vapors are detected.

The water, caustic, sugar, and allyl chloride are charged in that order, the mixture being cooled below 113° F. before addition of the allyl chloride to prevent its vaporization. In several runs in which the water had previously been saturated with caustic, little or no additional cooling was required. The charge is heated to 180° F. by water at about 200° F. in the jacket. When the pressure reaches 4 pounds per square inch, the reactor is vented briefly through a condenser to remove air. The pressure rises to about 29 pounds per square inch at 180° F.

Reaction can start almost immediately at 176° F., but there is

¹ Sugar Research Foundation.

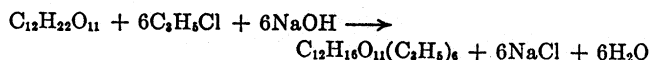
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TABLE I. PILOT PLANT

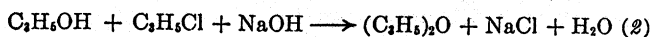
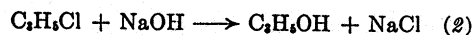
Run No.	Neutralized with CO ₂					Neutralized with H ₂ SO ₄				Neutralized with H ₃ PO ₄		
	20	21	22	23	27	24	25	26	31	30	32	33
Charge, % of capacity ^a	67	67	67	67	80	67	67	67	67	67	67	67
Reaction time, hours	4.7	5.8	6	6	6.1	6	5	6	4.7	5.7	6.1	5.4
Steam distillation												
Water added, lb.	0	0	5	5	0	0	0	0	3	0	0	0
Max. temp., ° F.	225	217	217	217	214	235	208	216	212	221	215	219
Neutralization		Before and during distn. ^c	Before distn.	Before and during distn. ^c	Before and after distn.	Before and during distn. ^c	After distn.	Before distillation				
pH after neutralization	6.8	..	7.3	7.6	6.5	6.8	7.2	7.4	7.1	8.0
pH before vacuum drying	7.4	8.6	6.5	7.2	..	7.0
Vacuum drying												
Vacuum, inches Hg	25	26.4	27.5	28.0	27.8	27.6	28.3	28.0	28.2	27.6	28.3	28.2
Final temp., ° F.	205	184	180	185	176	165	204	194	163	145	170	140
Product, lb. unfiltered	34.2	..	32.8	32.8	32	29.6	32.9	35.4	27.9	31.3	31.2	34.0
Filtration												
Filter aid, %	0.9	1.2	1.5	1.76
Av. temp., ° F.	140	95
Pressure, lb./sq. inch	15	15	15	15	15	15	15	15	15	15	15	15
Time, hours	3.5	1.42	0.75
Lb. product/ft. ² filter area	24.3	24.3	26.9
Product												
Color, Gardner	11.5	8.5	9.5	11.5	8	8	11	9	9.5	9	6	7
pH (10 × H ₂ O)	8.2	7.3	7.5	8.2	9.4	9.8	7.3	6.1	4.3	8.2	5	3.9
Allyl groups (based on OH)	6.3	6.7	6.2	6.1	6.6	6.2	6.3	6.6	6.2	6.9
Refractive index	1.4900	1.4902	1.4888	1.4899	1.4905	1.4900	..	1.4894	1.4899	1.4895
Viscosity, stokes	12.9	12.9	8.8	10.7-12.9	8.8-10.7
Gelation time ^f	114	164	147	250	233

^a Capacity charge is listed on Figure 3. ^b 50% excess NaOH added. ^c Added after steam distillation. ^d 5- to 6-inch vacuum used.

usually a delay in this kettle—averaging 1.5 hours—before reaction is indicated by an increase in pressure and temperature. During this period, there is little mixing of the two liquid phases. Once reaction starts, admixture increases greatly, and considerable heat is liberated. Cooling water is used in the jacket to maintain a temperature of about 180° F. throughout the reaction period. When the reaction begins in a charge containing 33 pounds of sugar, it is necessary to use water at about 135° F. in the 5.3-square foot jacket to keep the temperature at 180° F. As the reaction proceeds, the heat liberation rate falls off and is low after 6 hours, at which time the reaction is essentially complete and the pressure has dropped to about 15 pounds per square inch. The exact substitution varies slightly, but the following equation represents the reaction for a substitution of six allyl groups:



During the reaction, allyl alcohol and allyl ether are also formed in the reactor as follows:



Reduction in the amount of allyl chloride brought about by formation of these materials causes the gradual drop in pressure during the reaction.

After completion of the reaction, the pressure is released through the condenser, flashing off a portion of the volatiles. Preliminary work has indicated that this fraction, which contains about half the excess allyl chloride along with small amounts of allyl alcohol and allyl ether, might be re-used directly as part of the allyl chloride for a subsequent run.

The reaction mixture is then washed with 125 pounds of water to remove most of the excess sodium hydroxide and the sodium chloride formed during the reaction. The mixture is agitated for several minutes and then allowed to settle for at least 30 minutes. The water layer, which is on the bottom, is drained off and discarded. This material contains enough allyl alcohol to present

a disposal problem but probably not sufficient to warrant recovery for its intrinsic value.

After addition of 45 pounds of water, the remaining volatiles are recovered by steam distillation. About 50 pounds of steam are required for heating and stripping. The added water reduces color formation during this step by diluting the residual caustic and salts. After the solution has been cooled to about 150° F. and allowed to settle, the supernatant water layer is carefully decanted. It contains a small amount of dark material, formed during the distillation, which must be removed before neutralization if a light product is to be produced.

The product, still containing 20 to 40% water in a stable emulsion, is neutralized with 0.1 to 0.2 pound of phosphoric acid (5% solution) to a pH of 7.2, as measured with a glass electrode in the emulsion. Such pH measurements of emulsions are not absolute, but they give a practical method of control.

The water in the product is evaporated under a vacuum of 28 inches of mercury by heating to about 140° F. with water at 200° F. in the jacket. The product must be thoroughly dried at this point.

Precipitated salts and other impurities are then removed by filtration of the warm product. By using about 2% of a moderately fast filter-aid, 3 to 4 gallons of allylsucrose can be filtered

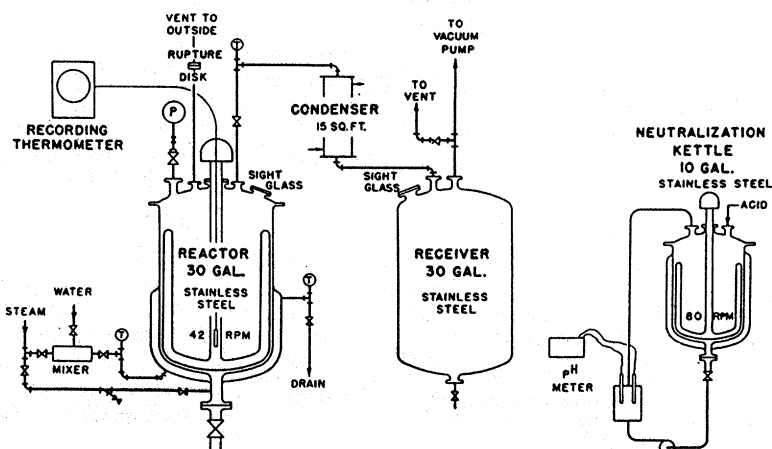


Figure 1. Equipment Used for Production of Allylsucrose

PRODUCTION DATA

Neutralized with H_2PO_4											
35	36	37	38	39	41	42	43	44	45	46	47
67	67	100	100	100	100	100	100	100	100	100	100
5.9	7.1	5.9	6.2	5.9	5.6	7.2	6.1	5.8	5.8	6.0	5.7
0	45 ^c	45	45	45	45	46	45	45	45	45	45
216	222	206 ^d	211 ^d	223	214 ^d	208 ^d	210 ^d	217	214	217	218
Before and after distn.						After distillation					
8.5	8.0	6.9	7.5	7.9	7.5	8.2	8.3	7.2	7.0	7.6	7.3
7.3	7.1	6.9	7.5	7.9	7.5	8.2	8.3	7.2	7.0	7.6	7.2
28.1	28.0	28.0	28.1	28.1	27.0	27.6	27.9	28.1	28.5	28.5	28.5
144	130	142	137	135	155	135	135	133	130	140	135
34.8	30.5	48.1	48.1	49.0	49.0	50.5	47.0	48.5	51.3	47.0	48.0
2.04	2.30	2.32	2.30	2.33	1.67	1.98	2.0	1.67	3.33	2.67	2.34
106	100+	106	130	110	110	110	112	115	134	150	150
15	15	15	15	15-25	15	25	25	25	25	25	25
2.7	1.23	6+	5.5	..	2.7	5.0	2.6	6.0	2.0	2.3	..
25.4	23.2	..	30.8	..	42.3	32.8	40.3	42.0	44.8	35.4	..
9	6	4.5	5.5	5	6.5	6.5	6	4.5	6.5	6	6
5.2	4.0	5.2	9.0	5.5	3.3	6.3	6.3	6.3	5.3	8.0	6.0
6.2	6.6	6.1	6.3	6.2	6.1	6.2	6.3	6.4	6.2	6.2	6.3
1.4920	1.4889	1.4880	1.4888	1.4888	1.4901	1.4889	1.4895	1.4898	1.4882	1.4895	1.4898
22.7-27.0	6.3-8.8	12.9	10.7-12.9	8.8-10.7	10.7-12.9	10.7-12.9	10.7-12.9	10.7-12.9	6.3	10.7	12.9
121	206	235	143	210	168	138	147	156	249	140	162

^c During vacuum drying. / At 100° C., 7.5 liters O_2 per hour.

per square foot of filter area before it is necessary to clean the filter.

PROCESS AND OPERATING VARIABLES

Table I gives the pilot plant data for all significant runs, grouped according to the neutralizing acid used. The "standard" process described was employed for run 37 and all subsequent runs. Earlier runs varied somewhat in their sequence of operations, as noted in the table. In some runs the reacted mixture was cooled by running water through the jacket, and volatiles were not flashed off.

Reaction. The effect of changing the proportions of the raw materials charged was not investigated systematically. However, in one run (33), in which 50% extra caustic was used, the reaction proceeded with unusual vigor, and in a second run (not completed), in which only 50% of the normal water was used, reaction proceeded less vigorously than normal.

The delay in reaction initiation, which ranged from about 1 to 3 hours in the 30-gallon reactor, was not encountered in smaller runs in the 1-gallon autoclave; hence, it probably can be eliminated.

Attempts to eliminate this delay included varying the order of charging the raw materials; purging the reactor with nitrogen to remove oxygen before the reaction; installing a baffle to increase the agitation; increasing the speed of the agitator from 45 to 78 r.p.m.; and using c.p. sodium hydroxide. None of these changes speeded reaction initiation consistently. Poor contact between the two liquid phases is the most probable cause of the lag, but this has not been proved, since in this kettle it was not practical to obtain enough agitation to cause good intermixture of the two liquids prior to reaction. When reaction starts, the resultant evolution of heat and vapors greatly increases the mixing action.

Product Purification. The sodium chloride, allyl ether, and allyl alcohol, formed during the reaction, and the residual raw materials must be removed to leave a clear dry neutral product. The allyl compounds in the flashed volatiles and the steam distillates, which contain about 48% of the allyl in the allyl chloride charged, are sufficiently valuable to warrant recovery. Recovery of the salt and caustic from any fraction would probably not be economically feasible.

Allyl by-products are recovered during flashing and steam distillation. Flashing the most volatile fraction at the conclusion of the reaction is a convenient method of releasing the final reaction

pressure and at the same time recovering a fraction rich in allyl chloride. In the earlier runs, this operation was omitted. The allyl compounds remaining after flashing are removed by steam distillation after washing and dilution of the residual caustic. Reduction of alkalinity prior to distillation is essential because heat discoloration is accelerated by high alkalinity. Less color is produced when the steam distillation is carried out after neutralization, but this complicates neutralization because hydrochloric acid is freed by hydrolysis of allyl chloride during steam distillation. In this case a second pH adjustment is usually required.

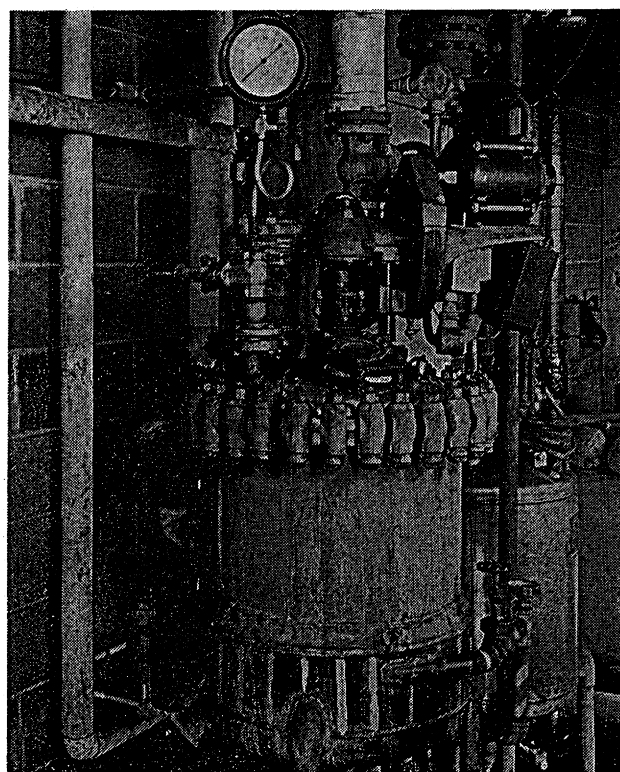


Figure 2. Allylsucrose Reactor

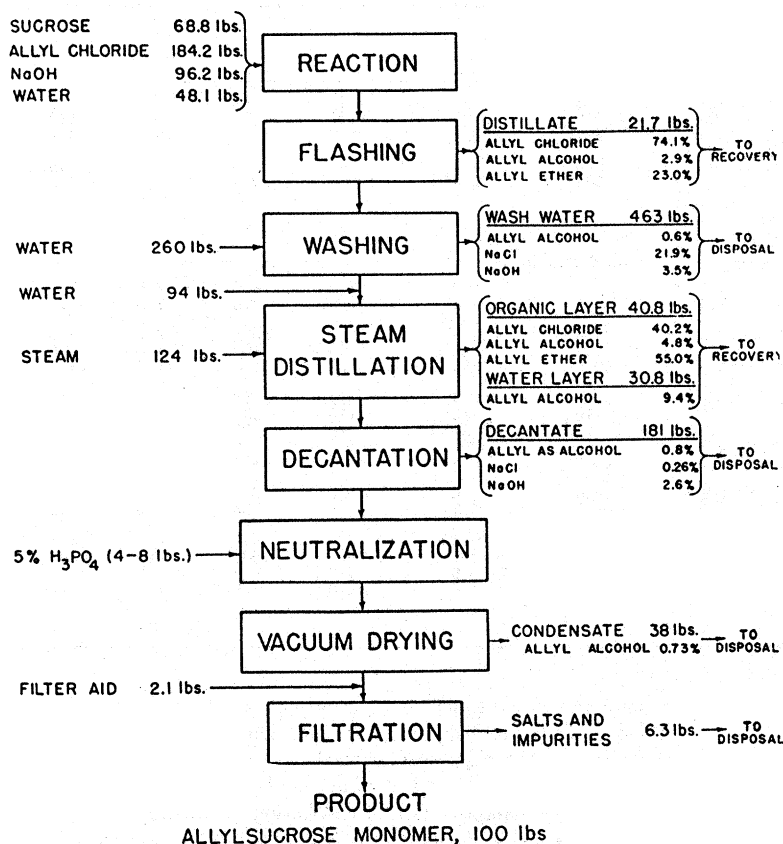


Figure 3. Allylsucrose Production Flow Sheet Based on 100 Pounds of Product

Allylsucrose forms a stable emulsion with 20 to 40% water. This property reduces the efficiency of separation of wash water and of decantation after steam distillation. After washing and steam distillation, most of the salt and caustic, not removed in the water wash, is removed with the water decanted after steam distillation.

After neutralization and vacuum drying, the product still contains a small amount of insoluble salts and polymerized material, which are removed in a pressure filter. Filtration rates increase with pressure up to at least 25 pounds per square inch, the highest pressure used, without apparent compacting of the filter cake. The temperature of filtration also has a significant effect on the filtration rate, because allylsucrose viscosity decreases appreciably with increase in temperature. Figure 4 shows the viscosity-temperature curve for a typical allylsucrose monomer. Many of the early filtrations were carried out at low temperatures in an effort to minimize product discoloration. It has since been shown by time-temperature tests that filtration at temperatures up to 170° F. produce no appreciable darkening. Filtration should therefore be carried out as close to this temperature as convenient. It will probably be practical to filter the dried product with little if any additional heating.

pH Control. The pH value of water-free allylsucrose cannot be measured directly because it is a nonpolar material, but arbitrary values were obtained by measuring the pH of an emulsion of the product with 10 times its weight of boiled distilled water. A neutral product was desired. The pH of purified allylsucrose as measured in this manner varies with the amount of water used. Figure 5 shows variation of pH measurement with dilution for three products in different ranges. Measurements of pH during neutralization do not vary greatly with dilution, however, probably because of the buffering action of the salts still present.

In almost all runs, the pH of the final product was less than

that to which the material was neutralized in the kettle. The removal of salts during filtration was at least partly responsible for this shift. This should be compensated for by neutralizing to a slightly higher end point than that desired in the product.

pH control was poor in the earlier runs, in which neutralization was carried out before steam distillation, and subsequent hydrolysis of allyl chloride occurred.

Pilot plant batches, neutralized with carbon dioxide or sulfuric acid, gave consistently darker products than those neutralized with phosphoric acid. In duplicate laboratory tests in which these acids, acetic acid, and hydrochloric acid were used, the phosphoric acid-neutralized allylsucrose was substantially lighter in color than the others.

Color Control. When allylsucrose is heated in the presence of a basic solution, a dark viscous material is formed. This material, which contains about 29% allyl groups and 2% hydroxyl groups, is soluble in basic water solutions but insoluble in a neutral water solution.

Producing a light product requires minimizing formation of this material and washing out as much of that formed as possible. To minimize color development, the temperature during the reaction should not exceed 185° F., and the temperature during steam distillation should be held to the minimum required to vaporize the allyl by-products. The water added prior to steam distillation helps reduce formation of color by dilution of the caustic still remaining and washes out most of the color formed. A slight improvement in color is obtained by steam distilling under a vacuum of

5 to 6 inches of mercury at a lower temperature, but the improvement in product does not appear to justify this procedure.

Gardner color standards are used to measure and compare allylsucrose color. Phosphoric acid-neutralized products as light as 4 and 5 have been produced in the pilot plant, but a Gardner color of 6 is a better average for such materials. The color also has been measured with a photoelectric colorimeter using a filter with a transmittance curve similar to that of the International Commission on Illumination Standard observer. Transmittance measurements of a series of allylsucrose samples by this means were in proportion to their Gardner color ratings established by

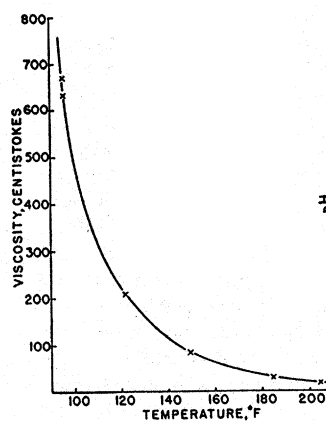


Figure 4. Variation in Viscosity of Allylsucrose Monomer with Temperature

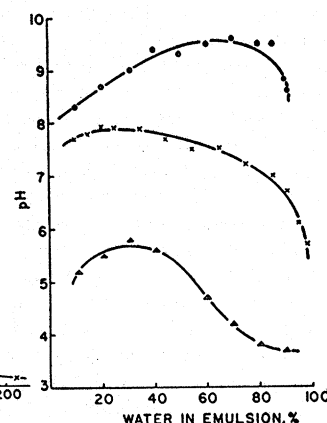


Figure 5. Variation in pH of Allylsucrose-Water Emulsions with Water Content

was determined experimentally in an Othmer equilibrium still (1). The allyl chloride fractions were determined by chloride analysis. Table V shows the data obtained. The small effect of the variation in total pressure is negligible for these approximate calculations. Liquid-vapor equilibrium data for the water-allyl alcohol system were obtained from a Shell Chemical Corp. publication (4).

TABLE V. ALLYL CHLORIDE-ALLYL ETHER EQUILIBRIUM DATA

Allyl Chloride, %		Boiling Point, ° C.	Atmospheric Pressure, Mm. Hg.
Liquid phase	Vapor phase		
6.43	24.55	86.6	749.8
10.97	38.1	81.7	743.1
16.84	50.9	76.6	748.5
21.65	59.5	72.8	749.0
28.4	68.0	68.9	767.0
34.45	75.4	66.0	767.0
50	81.1	60.4	768.0
51.9	83.6	56.5	762.8
70.3	93.4	51.9	761.2

DISCUSSION

A suitable method for producing allylsucrose monomer has been worked out in all essential parts in this pilot plant study. This method consistently produced good allylsucrose monomer of Gardner color 6 or lighter, a color which is considered quite satisfactory.

The process used to produce material for study has been described in considerable detail. The pilot plant equipment used was not specifically designed for the process, and operations were carried out in an 8-hour day, shutting down at night. Certain phases of this operation, therefore, were determined by the peculiarities of the available equipment and operation schedule, and there are a number of obvious improvements which a production plant could make. In handling the raw materials, the water and sugar could most readily be handled as a sugar solution. The heat of solution of the caustic could be used to heat the mixture if the water fraction were added last. No change in the reaction was observed in one run in which this was done. The reactor should have sufficient agitation to mix the two liquids and thus promote more rapid initiation of the reaction.

In a production unit, a cold water jacket would probably give insufficient cooling to control the reaction during its early stages. A supplementary reflux condenser could be used for this purpose. A separate unit should be used for all steps after flashing. This would permit use of a smaller reactor and would simplify the design of packing glands, because neither unit would be used for both pressure and vacuum. In a production plant, it would be economical to extract the allylsucrose from the final filter cake with acetone or some other solvent.

COST ESTIMATE

An estimate has been made of the cost of manufacturing allylsucrose. This is based on data obtained in the pilot plant on the process itself. The cost of solvent recovery, however, is estimated on the suggested method, which, as pointed out previously, is based on theoretical considerations only. Because the caustic soda, salt, and part of the allyl compounds are not recovered, there will be a waste disposal problem, but no allowance is made in the cost estimate for disposal of these wastes.

The basis is a factory producing approximately 2,500,000 pounds of allylsucrose per year. It is operated 300 days a year, with three shifts a day. The capital investment for such a plant would be approximately \$310,000, with an additional working capital of about \$45,000. Capital costs are listed in Table VI. A detailed cost sheet is given in Table VII. The "cost to make" would be about 34 cents per pound. This includes all items such as materials, labor, factory overhead, interest on working capital, and expenses for research, development, and administration, but it does not include selling costs. To arrive at the selling price, it is only necessary to allow for waste disposal and to add profit (including income tax) and selling expense.

TABLE VI. CAPITAL COSTS

Land and site preparation	\$ 3,500.00
Roads and parking areas	2,900.00
Railroad siding	2,700.00
Buildings	50,300.00
Boilers	21,000.00
Equipment, manufg.	76,000.00
Erection of equipment, manufg.	19,000.00
Instrumentation	3,800.00
Piping and ductwork	22,800.00
Erection of piping and ductwork	16,000.00
Heating, installed	2,100.00
Lighting, installed	2,000.00
Power, installed	2,700.00
Transportation facilities	3,800.00
Freight on equipment	1,500.00
Office furniture and fixtures	800.00
Contingencies	30,800.00
Engineering fees	48,300.00
Total fixed capital	310,000.00
Working capital	45,000.00
Total capital	\$355,000.00

TABLE VII. COST SHEET
(7200 operating hours per year)

	Cost/Day	
Material, lb.		
15,683 allyl chloride at \$0.15/lb.	\$2352	
5,858 sugar at \$0.05/lb.	293	
8,190 caustic soda at \$0.035/lb.	287	
179 phosphoric acid at \$0.05/lb.	9	
179 filter-aid at \$0.025/lb.	4	
198 acetone at \$0.115/lb.	23	\$2968
Credits, lb.		
2765 allyl chloride at \$0.15/lb.	\$415	
2335.2 allyl ether at \$0.22/lb.	514	
220.5 allyl alcohol-water at \$0.20/lb.	44	973
Total material cost		\$1995
Labor		168
Prime cost		\$2163
Indirect materials		
Containers (55-gallon drums at \$7.50), 17		128
Indirect labor		
Supervision	\$33	
Watchman, yardmen	6	
Mechanics, etc.	16	
Office help	23	
Truck operator	10	84
Indirect expenses		
Insurance, personal liability and fire	\$ 5	
Taxes	20	
Interest, fixed capital	51	
Social security	3	
Workmen's compensation	8	
Unemployment insurance	102	
Depreciation	100	
Maintenance, repairs and renewals	10	
Vacations	17	
Power	113	
Steam	22	
Water	6	
Gasoline	2	462
Factory supplies		\$2841
Factory cost		
Interest on working capital	\$ 8	
Research and development	37	
Adm. and general expense	37	82
Cost to make		\$2923
Cost/lb. to make (daily production, 8514 lb.)		\$0.34

ACKNOWLEDGMENT

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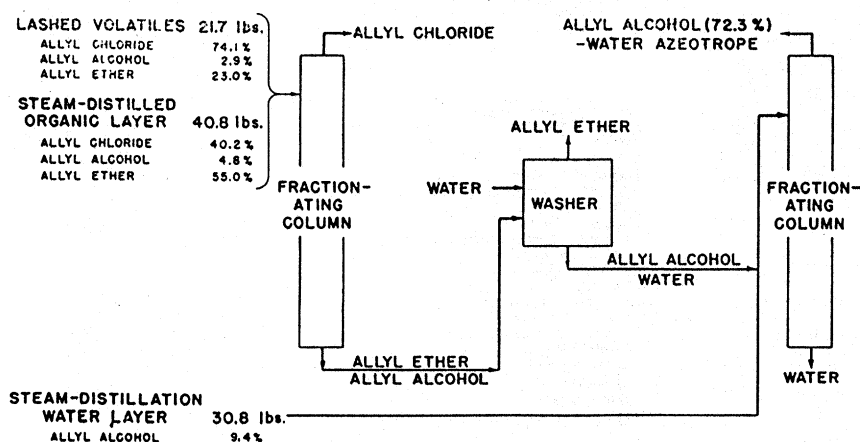


Figure 6. Possible By-Product Recovery System Based on 100 Pounds of Allylsucrose

visual comparison with standards but showed much greater absorption than the corresponding standard Gardner fluid.

Material Balance. Table II shows an average material balance for six pilot-plant runs. In most of these runs, the separate neutralization kettle was used; in these cases, material adhering to the kettle on draining was lost three times. In one run, in which neutralization was carried out in the reactor, the over-all yield was greatly increased, as shown under best pilot plant process (Figure 3). The product yields are based on the weight of dry unfiltered allylsucrose with a correction for the weight of solids removed and a 1% allowance for loss during filtration. It assumes recovery of product from the filter cake. In this pilot plant, actual yields were always lower because of high losses during filtration; such losses could be greatly reduced in a production unit where complete clean-out between runs could be omitted. Table III shows an actual filtration material balance.

Although the allyl loss is listed in Table II as allyl chloride, portions of the allyl loss can be accounted for in product losses and in polymerized allylsucrose monomer removed by the final filtration, as well as vapor losses.

TABLE II. PILOT PLANT MATERIAL BALANCE

	Average of 6 Runs	Best Pilot Plant Process ^a
Charge		
Sugar, lb.	33	33
Allyl chloride, lb.	88.5	88.5
NaOH, lb.	46.2	46.2
Water, lb.	23.1	23.1
Product before filtration, lb.	48.4	51.5
Product after filtration (calcd.), lb.	45	48
Yield, % of theoretical based on sugar	79	84.2
By-products		
Allyl chloride (total), lb.	15.6	..
Allyl alcohol (recoverable), lb.	2.6	..
Allyl in water layers to be discarded, as alcohol, lb.	2.3	..
Allyl ether, lb.	13.2	..
Allyl not accounted for, as allyl chloride, lb.	9.7	7.4

^a Neutralization carried out in reactor.
^b Corrected for excessive filtration loss.

TABLE III. SAMPLE FILTRATION MATERIAL BALANCE

	Pounds
Unfiltered product	46.1
Filtered product	37.1
Product recovered from cake	1.5
Product recovered from filter	2.6
Water-soluble salts recovered	1.2
Water insolubles recovered	1.4
Losses (leakage, holdup, etc.)	2.3

Additional increase in product yield would be expected in a production unit, because holdup from one run would be largely recovered in the next.

BY-PRODUCT RECOVERY

Recovery and utilization of the allyl by-products will be an important economic consideration in this process. As shown in Figure 3 and Table IV, allyl compounds other than allylsucrose monomer appear at five different stages of the process. In three of these—the wash water, the decantate after steam distillation, and the water removed during vacuum drying—the allyl content is so low that its recovery is probably not practical. The flashed and steam distilled volatiles, however, contain large amounts of allyl chloride, allyl ether, and allyl alcohol.

TABLE IV. BY-PRODUCT YIELD AND COMPOSITION

	Allyl Chloride, Lb.	Allyl Alcohol, Lb.	Allyl Ether, Lb.	NaOH, Lb.	NaCl, Lb.	% of Total Allyl Charged
Charge	88.5	100
By-products						
Flashed volatiles	7.70	0.30	2.40	13.4
Wash water	..	1.35	..	7.8	48.9	2.0
Steam distillate—organic layer	7.91	0.93	10.76	29.3
Steam distillate—water layer	..	1.35	2.0
Decantate after steam distillation	..	0.80	..	0.23	2.3	1.2
Drying condensate	..	0.13	0.19
Total by-products	15.6	4.86	13.2	8.0	51.2	48.1

No pilot plant study was made on recovery of these allyl by-products, but a recovery method, based on theoretical considerations only, is suggested in Figure 6. It may be possible to recycle the flashed volatiles back into the reactor charge without further concentration of the allyl chloride, but since this has not been proved it is merely suggested as a possibility.

In the suggested allyl by-products recovery method, the flashed volatiles and the steam distillate organic layer are combined, and the allyl chloride is distilled off. High purity of the allyl chloride fraction is unnecessary, because it is to be re-used in the process. The allyl alcohol is then washed from the allyl ether fraction with water, combined with the steam distillate water layer, and distilled in a fractionation column. This produces a water-allyl alcohol azeotrope containing 72.3% allyl alcohol (2), which may be marketable in that form. If more concentrated allyl alcohol is required, it can be obtained by extractive distillation with allyl ether as described by Fairbairn *et al.* (2).

Calculations of the approximate number of theoretical stages required for the fractionation columns were made by the McCabe-Thiele method (3). The allyl chloride and allyl alcohol fractionation columns each require approximately six theoretical stages at reflux ratios of 2 and 3, respectively. The exact design of each column is, of course, somewhat flexible, because the most desirable reflux ratio depends on economic considerations.

The effect of the small amount of allyl alcohol present was neglected in calculations for the allyl chloride column. Because no literature reference could be found for the liquid-vapor equilibrium curve for the allyl chloride-allyl ether system, this curve